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THE EFFECT OF ORIENTED DEFECTS ON LONG-RANGE ORDERING
OF HYDROCARBON FILMS: AZULENE ON Pt(111)

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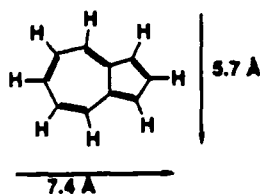
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In the present work we have used low energy electron diffraction (LEED) to investigate the effect of ion bombardment-induced defects on the long-range ordering of azulene molecules adsorbed on Pt(111). These defects result in preferred directional ordering of the organic film as demonstrated by the stabilization of certain domains over others.

Azulene ($C_{10}H_8$) is a partially aromatic isomer of naphthalene, consisting of fused seven-member and five-member carbon rings. The molecule is essentially planar and has the structure and dimensions shown below:



At monolayer saturation on Pt(111), azulene packs in an ordered structure with a molecular spacing of three platinum atoms [1-3]. This is consistent with the size of the molecule if the molecular plane is parallel to the surface. Thermal desorption experiments result in the evolution of only H_2 above $180^\circ C$, indicating molecular adsorption at room temperature [2]. Azulene is a large enough molecule that in a close-packed overlayer structure it interacts with nine surface platinum atoms; consequently, the bonding of azulene to Pt(111) is relatively non-site specific.

Room temperature adsorption of azulene at coverages within the range of $1 < C/Pt < 1.3$ results in domains of ordered molecules. These domains have random rotational orientation on the platinum substrate. One such domain in which the azulene molecules are aligned with the platinum substrate is shown in Figure 1. Apparently, the bond energy of azulene on smooth Pt(111) is independent of the rotational alignment of the molecule; hence, the individual domains are expected to be randomly oriented. The azulene domains have the same internal structure and should thereby be found with equal probability on the surface since they have the same structural energy. This was noted by the retention of a continuous $1/3$ order ring in the



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azulene/Pt(111) LEED pattern throughout the annealing process. Ordering of the domains was achieved, however, by bombarding the Pt(111) surface, prior to azulene adsorption, with 500-eV argon ions at an angle of incidence of 45° off-normal in the $\langle\bar{1}10\rangle$ direction. Bombardment of the surface in such a manner introduces oriented defects, defects which limit domains to those in energetically stable alignment with the preferential $\langle\bar{1}10\rangle$ direction. This directionality was manifested by segmentation of the previously observed $1/3$ order ring in the azulene LEED pattern into well-defined (though diffuse) $1/3$ order diffraction beams. Experiments in which the ion beam was incident normal to the surface showed no preferential directionality.

In these experiments, typical ion dosages were $2 \mu\text{A}$ for 300 seconds, or approximately 4×10^{15} ions/cm². Immediately after bombardment of the clean surface, the sample was annealed for 300 seconds at 875 K to remove carbon remaining after the sputtering process. Subsequent LEED patterns of the damaged Pt(111) surface showed only a slight increase in the diffuse background and very minor broadening of the diffraction beams. Even higher temperature annealing of the surface for short time periods did not completely remove the defect-induced directionality, which reflects the extent of the defect stability. Adsorption of azulene onto the bombarded substrate after it was cleaned in oxygen and annealed at 1273 K for 120 seconds, resulted in a LEED pattern for which the segmentation of the $1/3$ order diffraction features was only slightly diminished.

To determine the effect that the azimuthal angle of the incident ion beam has on the orientation of the azulene domains, the Pt(111) surface was bombarded along the $\langle\bar{1}\bar{1}2\rangle$ direction. The resulting LEED patterns showed that the most stable domain orientation was that which was in alignment with the $\langle\bar{1}10\rangle$ direction of the substrate, the same finding reported for azulene adsorbed on a substrate bombarded along the $\langle\bar{1}10\rangle$ direction. It appears that the position of the incident ion beam relative to a particular azimuthal direction of the surface has no effect on the rotational alignment of the azulene domains.

Evidently, modification of surface morphology contributes to the ordering of the azulene domains. For a Pt(111) surface, the lateral distribution of ion bombardment-induced defects through the formation of vacancy clusters and the alignment of resulting steps along close-packed and energetically favorable directions has been verified by helium atom scattering techniques [4,5]. These studies lend support to our observations that the defects introduced by off-normal incidence ion bombardment may be preferentially oriented. Furthermore, the limitation of defects to close-packed directions may account for the fact that bombarding along a $\langle\bar{1}\bar{1}2\rangle$ direction of our Pt(111) surface yields the same type of azulene ordering as bombarding along a $\langle\bar{1}10\rangle$ direction; upon annealing, the defects align along the more stable direction. The effect that the incident polar angle of the ion beam relative to the substrate has on the distribution of bombardment-induced defects has yet to be investigated by helium scattering.

It appears that the preferentially-oriented defects bring about domain ordering by offering anchoring sites for azulene molecules. Since the intermolecular forces are greater than those between an azulene molecule and a flat terrace of the platinum substrate, alignment of just a few azulene molecules along a defect may influence other molecules to conform to this orientation. The result is the preferential ordering of domains over most of the surface as indicated by 1/3 order ring segmentation.

Experiments have also been conducted on the stepped Pt(S)-[16(111)x(100)] surface. The steps generate a slight directionality preference as evidenced by slight segmentation of the 1/3 order diffraction features of the azulene overlayer. Segmentation, however, was not as distinct as in the case of the asymmetrically bombarded surfaces.

In progress are experiments in which the off-angle bombardments in the $\langle\bar{1}\bar{1}2\rangle$ direction are performed without subsequent annealing, thereby preventing platinum

atoms from migrating to sites along the $\langle \bar{1}10 \rangle$ direction. By so doing, the possible azimuthal dependence of the incident ion beam on preferential alignment of defects may become apparent. More extensive experiments involving the study of the ordering behavior of azulene domains as the number of anchoring sites is progressively decreased are also planned.

In summary, this work shows that off-normal incidence ion bombardment-induced defects can lead to a directionality of a nominally smooth surface resulting in stabilization of particular domains of molecular adsorbates. Furthermore, the "directionality" of the surface is not easily removed by high temperature annealing. Our observations show a strong dependence on the orientation of the polar angle of the incident ion beam. Although the observed lack of sensitivity to the incident azimuthal angle of the ion beam is consistent with interpretations of helium scattering data [5], the simple concept that annealing arbitrary ion bombardment-induced defects to give close-packed facets is not consistent with the lack of directionality which we observe following normal incidence bombardment.

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FIGURE CAPTION

Figure 1. Model of an azulene domain indicating the closest-packed nature of the overlayer if the molecular plane is parallel to the platinum surface.

